Message

From: Detlef Knappe [knappe@ncsu.edu]
Sent: 3/11/2018 10:18:21 PM
To: Strynar, Mark [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=5a9910d5b38e471497bd875fd329a20a-Strynar, Mark]; Lindstrom, Andrew [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=04bf7cf26aa44ce29763fbc1c1b2338e-Lindstrom, Andrew]; McCord, James [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=McCord, James]
Subject: Gordon Research Conference

Andy, Mark, and James,
I submitted the following poster abstract to the Gordon Research Conference with you as co-authors. Also Zack and Chuhui.
Let me know if you see issues.
Best,
Detlef

Enhanced total oxidizable precursor assay for perfluoroalkyl ether acid chemistries

Per- and polyfluoroalkyl substances (PFASs) are anthropogenic chemicals that are used as surfactants and in firefighting foams, oil- and water-repellent coatings, and consumer products. Two long-chain PFASs, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), were historically produced in large quantity and have been widely detected in human sera and wildlife. A manufacturing shift towards short-chain PFASs and fluorinated alternatives started in the early 2000s when the U.S. and Europe took steps to limit the production and import of PFOS and PFOA. As a result, many new proprietary PFASs have been introduced to the market. Also, many PFAS chemistries include functional groups that can degrade in natural and engineered systems to dead-end products such as perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs). To quantify concentrations of unidentified precursors of PFSAs and PFCAs, the total oxidizable precursor (TOP) assay was developed. In the TOP assay, aqueous samples are exposed to hydroxyl radicals generated by thermolysis of persulfate at pH >12. In the process, many precursor compounds are oxidized to PFSAs and PFCAs that can be readily quantified by existing analytical methods. To date, no information is available about the fate of a recently discovered perfluoroalkyl ether acids (PFEAs) in the TOP assay.

The aims of this research are to (1) determine the fate of four perfluoroether carboxylic acids [perfluoro-2-methoxy acetic acid (PFMOAA), perfluoro-3-methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), and perfluoro-2-propoxypropanoic acid (PFPrOPrA = "GenX")], one polyfluoroether carboxylic acid (ADONA), and two polyfluoroether sulfonic acids (Nafion by-products 1 and 2) in the TOP assay and (2) assess whether PFEA precursors are important contributors to the total PFAS concentration in environmental waters near a fluorochemical manufacturer. Results obtained to date illustrate that PFPrOPrA is stable in the TOP assay and thus represents a new dead-end product that needs to be added to the list of target analytes for the top assay. We hypothesize that the other three perfluoroalkyl ether carboxylic acids will be similarly stable in the TOP assay, while the polyfluoroalkyl ether acids may be oxidized. For polyfluoroalkyl ether acids that exhibit reactivity, high resolution mass spectrometry will be used to identify reaction products. Once new dead-end products are identified and added to the list of target analytes for the TOP assay, the expanded TOP assay will be applied to assess whether precursors of the new target analytes are present in environmental waters near a fluorochemical manufacturer. The results of this study are expected to provide an enhanced TOP assay that will capture a larger fraction of oxidizable precursors that may be present in environmental samples.